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COMPLETE SPECIFICATION

A Process for the Preparation of Terephthalic Acid having Extremely High Purity

We, MITSUI PETROCHEMICAL INDUSTRIES, LTD., a joint stock company organized under the laws of Japan, of 1, No. 12, 1-Chome, Yuraku-cho, Chiyoda-ku, Tokyo, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a process for the preparation of terephthalic acid having extremely high purity.

Although it is well known to manufacture terephthalic acid by the oxidation of p-substituted aromatic compounds in a liquid phase, the obtained product contains still a small amount of impurities. In order to remove these impurities from the terephthalic acid various purifying methods such as the washing and recrystallization have been proposed, but it is impossible to completely remove the impurities. Hence it has been taken for the manufacture of polyester for fibre and film manufacturing a process wherein the terephthalic acid is once converted to dialkyl terephthalate and the latter is purified and then is ester-interchanged with glycol.

The object of the present invention is to provide a process for the manufacture of extremely high pure terephthalic acid by the oxidation in a liquid phase of p-substituted aromatic compounds and thereby it is possible to produce the terephthalic acid having such high purity as suitable for the manufacture of fibre or film forming polyester in which the terephthalic acid is directly reacted with glycol.

When the p-substituted aromatic compounds are oxidized with gaseous molecular oxygen in liquid phase and the obtained terephthalic acid is separated from the solvent, coexisting impurities such as aldehydes, ketones and other impurities, particularly unknown colored and color-forming impurities, are very difficult to separate from the terephthalic acid, because they are contained in the terephthalic acid crystals in a state in which they have been bonded with the crystallized terephthalic acid. If the oxidation temperature of p-substituted aromatic compounds is higher the contents of aldehydes or ketones in the obtained terephthalic acid are smaller, but on the other hand a side-reaction occurs. Therefore, the reaction time (that is the time for absorbing oxygen) is rather long, the yield of terephthalic acid is decreased and the product is extremely colored into yellow or yellowish orange.

According to the present invention, there is provided a process for the preparation of terephthalic acid wherein a p-substituted aromatic compound is catalytically oxidized with gaseous molecular oxygen in the presence of aliphatic carboxylic acid as a solvent and an oxidation catalyst as set forth hereinunder, and bromine or bromine compounds, characterized in that after the completion of oxidation reaction, the reaction mixture is further catalytically oxidized with gaseous molecular oxygen at a temperature of 200 to 300°C., which is higher than the previous oxidation temperature. According to the present process, the reaction intermediates and by-products in the reaction system may be completely oxidized and especially the impurities which are contained in the formed terephthalic acid may be oxidized or oxidatively decomposed at the same time, thus the highly pure terephthalic acid is obtained in a high yield.

The p-substituted aromatic compounds which are used in the process of the present invention as a raw material include dialkylbenzenes of which two alkyl radicals were substituted to the aromatic nucleus, for ex-

ample, p-xylene, p-methylethylbenzene and p-cymene and their derivative, for example p-tolylaldehyde, terephthalaldehyde, p-methylbenzyl alcohol, p-methylbenzyl chloride and p-tolylmethylketone; alkylaryl radical substituted alkylbenzenes such as p-tolylethane; p-substituted aromatic acids in which the substituent can be changed to carboxyl radical by oxidation such as toluic acid; or p-substituted benzoin in which the substituent can be changed to carboxyl radical by oxidation.

As the molecular oxygen, pure oxygen gas or a molecular oxygen containing gas especially air may be preferably employed.

As the catalyst, one or more of the oxidation catalysts used in the prior art, for example cobalt, manganese, chromium, nickel, cerium and lead may be employed. The form of the catalyst is not limited but it is necessary that the catalyst is soluble in the reaction system such as carboxylates and naphthenates of the metal. Further it is necessary that bromine or bromine compounds which are used together with said oxidation catalyst are also soluble in the reaction system, for example it is used in the form of bromine itself, hydrobromic acid, ammonium bromide, benzyl bromide and dibromoethane. And also said metal and bromine may be used in the form of for example manganese bromide and cobaltous bromide. The amount of catalyst and the bromine used are suitable in the range of about 0.005 to 10% by weight, especially 0.01 to 5% by weight based upon the p-substituted aromatic compounds, respectively.

As the solvent, it is suitable to use aliphatic carboxylic acid having 2 to 5 carbon atoms in the molecule. The amount of solvent used is suitable that it is sufficient to finally dissolve the terephthalic acid into the solvent. When the amount of solvent used is insufficient, the solvent is further added in necessary amount to dissolve the reaction mixture thereto after the completion of terephthalic acid manufacturing step and thereafter the 2nd step oxidation treatment of the present invention, that is the oxidation treatment of impurities may be carried out. This 2nd step oxidation treatment may be preferably carried out by using the solvent which contains up to about 20% by weight of water. The presence of water is preferable in order to protect a danger of explosion and to decrease a decomposition of solvent. Particularly when the water is present in an amount of 2 to 15% by weight, good results may be obtained for the decoloring and purification of terephthalic acid. This water may be supplied in the form of water itself or steam to the reaction system and also in the form of aqueous aliphatic carboxylic acid which was prepared by adding the water so as to maintain at a concentration within said range.

The process of the present invention is illustrated by the case in which highly pure terephthalic acid is manufactured from para-xylene. The para-xylene is oxidized with air in a liquid phase at a temperature of about 210°C., in the co-existence of cobaltous acetate, manganese acetate and ammonium bromide by using acetic acid as a solvent. In this case, the yield of terephthalic acid is normally at least 85 mol %, the content of aldehyde is more than 0.3% by weight and Hazen number in sodium hydroxide solution of it is more than 30. Even when the reaction product is contacted with molecular oxygen at the same temperature after the completion of above reaction, improvements of yield and degree of coloring are not recognized. When the paraxylene is first oxidized at the high temperature which is employed in the present invention, for example 250°C., a considerable side-reaction occurs and thus the yield of terephthalic acid formed is decreased to less than 70 mol % and the degree of coloring of it reaches a Hazen number in sodium hydroxide solution of 5,000 to 9,000. The "degree of coloring" represented by the Hazen number means the color of a solution in which 2.5 g. of the sample is dissolved in 100 ml. of 1 N aqueous sodium hydroxide, which is represented by American Public Health Association Color, (see Standard Method of Test for Platinum-Cobalt Color of Clear Liquids, American Society for Testing Materials, D 1209—54). The yield and degree of coloring are not practically improved even when said reaction product is contacted with a molecular oxygen at the same temperature after the completion of the previous reaction. According to the present invention, after the para-xylene was treated in a liquid phase by a normal reaction conditions of the manufacture of terephthalic acid, namely at a temperature of 170 to 230°C., when the temperature of reaction mixture is increased to a temperature of 200° to 300°C., preferably 230° to 280°C. which is higher than said reaction temperature and then the reaction mixture is contacted with a molecular oxygen, the yield, the content of aldehydes in the terephthalic acid and Hazen number of the obtained terephthalic acid are more than 88 mol %, less than 0.001% by weight and less than 10, respectively. Thus it is possible to obtain a terephthalic acid of very good quality which is possible to manufacture a polyester by the direct reaction of it with glycol. In order to avoid the danger of explosion, inert gas and/or steam can be added to vapour phase in the reaction system.

The process of the present invention may be carried out by a batch or continuous operation.

The present invention is illustrated by the following Examples and Comparative examples.

EXAMPLE 1

17 g. of para-xylene, 240 g. of commercial acetic acid, 0.05 g. of cobalt acetate, 0.1 g. of manganese acetate and 0.05 g. of ammonium bromide were charged into a titanium-lined autoclave with electromagnetic stirrer provided with a reflux condenser. The reaction mixture was heated at the temperature of 210 to 215°C. The pressure of autoclave was maintained at the pressure of 27 kg./cm^2 (gauge) by the introduction of air at the rate of 100 l./hr. while an evacuation was continued. The reaction was stopped when the concentration of oxygen in the exhausted gas reached the same concentration of introduced air.

Then the reaction mixture was heated up to the temperature of 250°C. with agitation the pressure was elevated to 35 kg./cm^2 (gauge) by supplying air and further air was introduced at the rate of 100 l./hr. while the evacuation was continued. After one hour, the introduction of air was stopped and the autoclave was naturally cooled to a room temperature. The obtained terephthalic acid was separated from the reaction mixture and the separated terephthalic acid was washed with acetic acid and dried to give 24.3 g. of white needle solid.

COMPARATIVE EXAMPLE 1

After a reaction was carried out by using the same raw material and at the same reaction conditions as Example 1, the temperature of the reaction was not increased but the pressure of the reaction was pressed to 35 kg./cm^2 (gauge) by supplying air and air was introduced at the rate of 100 l./hr. into the reaction mixture at the temperature of 210°C. with agitation, while the evacuation was continued. After one hour, the introduction of air was stopped and the autoclave was naturally cooled to a room temperature to obtain 23.3 g. of white terephthalic acid.

The results of Example 1 and Comparative example 1, were shown in the following Table 1.

TABLE 1

	EXAMPLE 1	COMPARATIVE EXAMPLE 1
Appearance	White needle solid	White solid
Purity (% by wt.)	100	98
Acid value	675	672
Aldehyde (by wt.)	Not detected	0.10
Hazen number in sodium hydroxide solution	5	More than 30

EXAMPLE 2

An oxidation in the first step of Example 1 (that is the oxidation reaction into terephthalic acid of raw material, para-xylene) was carried out by using the same raw material and at the same conditions as in Example 1. After the completion of reaction, the reaction mixture was added with 10 g. of water and the temperature of it was raised to the temperature of 250°C. with agitation and the pressure was pressed to 40 kg./cm^2 (gauge) by supplying air and air was introduced at the rate of 100 l./hr. into the autoclave while the evacuation was continued. After one hour, the introduction of air was stopped, the reaction mixture was naturally cooled to a room temperature. The formed terephthalic acid was separated from the reaction mixture. The separated terephthalic acid was washed with acetic acid and dried to give 24.3 g. of white needle solid. The obtained terephthalic acid had the purity of 100%, the acid value of 675, Hazen number of less than 5, and aldehyde was not detected.

COMPARATIVE EXAMPLE 2

The air-oxidation in Example 1 was carried out by maintaining the reaction temperature at the temperature of 250°C. instead of 210° to 215°C. When the concentration of oxygen in an exhausted gas was reached to constant value which corresponds to the concentration of oxygen in the supplied gas, the air-oxidation was further continued at that temperature for 60 minutes and then terephthalic acid was obtained by the same method as described in Example 1. The yield, the purity, the content of aldehyde and Hazen number were 60 mol %, 98%, 0.03% and 2500, respectively.

EXAMPLE 3

35 g. of para-xylene, 140 g. of commercial acetic acid, 0.088 g. of cobalt acetate, 0.1 g. of manganese acetate and 0.088 g. of benzyl bromide were charged into a 500 ml. autoclave with electromagnetic stirrer provided with a reflux condenser, the reaction mixture was heated at the temperature of 210° to 220°C. The pressure of autoclave was maintained at the pressure of 27 kg./cm^2 (gauge) by the introduction of air at the rate of 100 l./hr. while an evacuation was continued. The reaction was stopped when the concentration of air in the exhausted gas was reached to the same concentration of introduced air and the autoclave was naturally cooled to a room temperature. This re-

action mixture was a yellow slurry which contains yellowish solid of crude terephthalic acid. This reaction mixture was added with 300 g. of 98% acetic acid. The mixture was charged into a 1 l. titanium-lined autoclave with electromagnetic stirrer provided with a reflux condenser and air was introduced into the autoclave in the rate of 100 l./hr. with agitation so as to maintain the reaction pressure at 37 kg/cm^2 (gauge). After one hour, the introduction of air was stopped and the autoclave was naturally cooled to a room temperature and thereafter the reaction mixture was withdrawn from the autoclave, the reaction mixture was suction-filtrated to give 50.4 g. of white needle solid of terephthalic acid. The obtained terephthalic acid had the purity of 100% by weight (Barium salt method), the content of aldehyde of less than 0.001% by weight and Hazen number of less than 7.

WHAT I CLAIM IS:—

1. A process for the preparation of terephthalic acid wherein a p-substituted aromatic compound is catalytically oxidized with gaseous molecular oxygen in the presence of aliphatic carboxylic acid as a solvent and in the co-existence of an oxidation catalyst as hereinbefore set forth and bromine or bromine compound, characterized in that after the completion of oxidation reaction, the reaction mixture is further catalytically oxidized with gaseous molecular oxygen at a temperature of 200 to 300°C. which is higher than the previous oxidation temperature.

2. A process as claimed in Claim 1 wherein after the completion of oxidation reaction, the temperature of the reaction mixture is increased to a temperature of 230 to 280°C. which is higher than the previous oxidation temperature and further is contacted with gaseous molecular oxygen.

3. A process as claimed in Claim 1 wherein the whole reaction is carried out in a liquid phase.

4. A process as claimed in Claim 1 wherein the p-substituted aromatic compound is p-substituted aromatic hydrocarbon.

5. A process as claimed in Claim 1 wherein the oxidation catalyst is a metal or metal compound which is soluble in the reaction system.

6. A process as claimed in Claim 5 wherein the metal is cobalt and/or manganese and/or chromium.

7. A process as claimed in Claim 1 wherein the aliphatic carboxylic acid is acetic acid.

8. A process as claimed in Claim 1 wherein after the completion of oxidation reaction, the aliphatic carboxylic acid in the reaction system contains water of less than 20% by weight.

9. A process as claimed in Claim 8 wherein the content of water is 2 to 15% by weight.

10. A process as claimed in any Claims 8 and 9 wherein after the completion of oxidation reaction, the water is added in the form selected from the group consisting of water, steam and an aqueous aliphatic carboxylic acid into the reaction system.

11. A process as claimed in Claim 1 wherein after the completion of the oxidation reaction, the reaction mixture is dissolved in an additional amount of aliphatic carboxylic acid or aqueous solution thereof and the temperature of the solution is elevated and is again treated with gaseous molecular oxygen.

12. A process as claimed in Claim 1 wherein the gaseous molecular oxygen is air.

13. A process as claimed in Claim 1 wherein the pressure is sufficient to maintain the reaction system in a liquid phase at the reaction temperature.

14. A process for the preparation of terephthalic acid having extremely high purity as set forth in any one of Examples 1 to 3 herein.

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